

OXIDATIVE ADDITION OF SOLUBLE IRIIDIUM AND RHODIUM COMPLEXES
TO CARBON-HYDROGEN BONDS IN METHANE AND HIGHER ALKANES (1)

Andrew H. Janowicz, Roy A. Periana, J. Michael Buchanan,
Caroline A. Kovac, Jeffrey M. Stryker, Michael J. Wax and
Robert G. Bergman*

Materials and Molecular Research Division, Lawrence Berkeley
Laboratory, and Department of Chemistry, University of
California, Berkeley, California 94720, U.S.A.

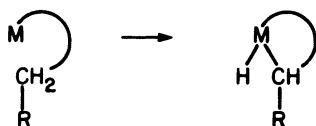
Abstract - A new type of iridium complex has been synthesized which successfully converts alkanes into hydridoalkylmetal complexes ($M + R-H \rightarrow R-M-H$). This material has the general formula $Cp^*(L)IrH_2$, where $Cp^* = \eta^5-C_5Me_5$, and $L = PMe_3$ (or, in a few cases, related phosphines). Upon irradiation with ultraviolet light, the dihydride loses H_2 , generating the reactive intermediate Cp^*IrL , which reacts rapidly with C-H bonds in every molecule so far investigated (including alkanes), leading to hydridoalkyliridium complexes $Cp^*(L)Ir(R)(H)$. Evidence has been obtained that this C-H insertion (oxidative addition) reaction proceeds through a simple three-center transition state and does not involve organic free radicals as intermediates. In accordance with this, the intermediate Cp^*IrL reacts most rapidly with C-H bonds having relatively high bond energies, such as those at primary carbon centers, in small organic rings, and in aromatic rings. This contrasts directly with the type of hydrogen-abstraction selectivity characteristic of organic radicals. The hydridoalkyliridium products of the insertion reactions can be converted into functionalized organic molecules--alkyl halides--by treatment with mercuric chloride followed by halogens. Expulsion (reductive elimination) of the hydrocarbon from the hydridoalkyliridium complexes can be induced by Lewis acids or heat, regenerating the reactive intermediate Cp^*IrL , which is then capable of attacking the C-H bond of other hydrocarbons. This property has been used to examine the interconversion of different hydridoalkyliridium complexes. By determining the equilibrium constants for these interconversions, one obtains a method of estimating relative iridium-carbon bond energies. The equilibrations have also been used to devise a thermal method for activating methane. In this case, heating the cyclohexyl-(hydrido)iridium complex in cyclooctane under 20 atm of CH_4 produced a 58% yield of $Cp^*(L)Ir(CH_3)(H)$, which is the thermodynamically most stable C-H insertion product in this system. Oxidative addition of the corresponding rhodium complexes Cp^*RhL to alkane C-H bonds has also been observed, although the products formed in this case are much less stable, and undergo reductive elimination at -20° . These and other recent observations provide an incentive for reexamining the factors which have been assumed to control the rate of reaction of transition metal complexes with C-H bonds--notably the need for electron-rich metals and the close proximity of reacting centers.

INTRODUCTION

Organometallic chemists have been attempting for several years (2) to find a simple example of the intermolecular alkane carbon-hydrogen insertion (or "oxidative addition") reaction illustrated in the equation at the bottom of Scheme 1. They have been tantalized by the many intramolecular examples of this process (top of Scheme 1) (3), and frustrated by the fact that before

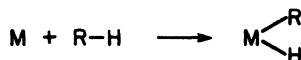
Scheme 1Homogeneous Saturated C-H Bond Activation:

Intramolecular:



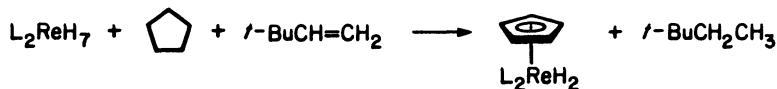
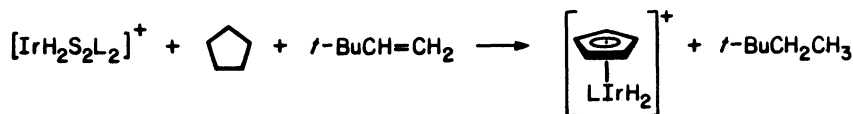
(Many examples)

Intermolecular:



(Few examples; none where R-H is a completely saturated hydrocarbon)

the work outlined here was reported, all attempts to extend these intramolecular observations to the corresponding intermolecular reactions had failed. However, several multi-step reactions which may well be initiated by intermolecular oxidative addition are known. Two of the most interesting and clean-cut of these examples, reported recently at Gif-sur-Yvette and Yale University (4), are shown in Scheme 2.

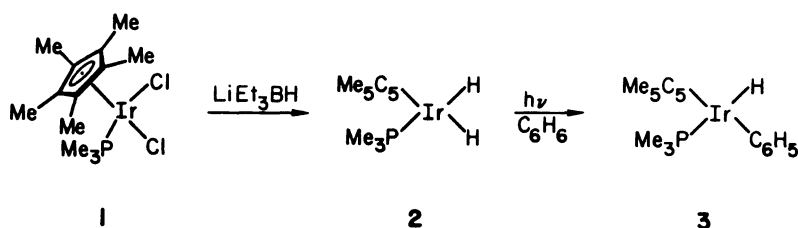
Scheme 2Baudry, Ephritikine, Felkin, 1980:(L = PPh₃, PEt₂Ph)Crabtree, Mihelcic, Quirk, 1979:(L = PPh₃, S = H₂O or acetone)

This lecture summarizes our discovery (5) and further investigation of a system which provides the first clear-cut example of the single-step intermolecular C-H oxidative addition reaction shown in Scheme 1, and discusses our preliminary studies of the nature of this reaction.

GENERATION AND OXIDATIVE ADDITION REACTIONS OF
($\eta^5\text{-C}_5\text{Me}_5$)(PMe₃)Ir

In connection with a project aimed at examining the products of hydrogenolysis of metal alkyls, we had occasion to prepare dihydridoiridium complex 2 by the reaction shown in Scheme 3. Many dihydridometal complexes are known to undergo reductive elimination of H₂ upon irradiation (6). In complexes

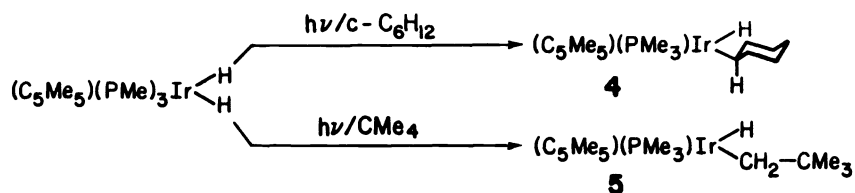
Scheme 3



related to 2 (e.g., Cp_2MoH_2 ; $\text{Cp} = \text{C}_5\text{H}_5$) the type of intermediates generated in such reactions have been shown to insert into at least some types of C-H bonds (7). We therefore decided to investigate the irradiation of 2. We were encouraged to find that in benzene only 3, the product of intermolecular C-H activation, was formed; no orthometallation product was observed. Benzene is well-known to be reactive toward C-H activation, presumably because of involvement of its π -electrons in the insertion transition state. Our next step, therefore, was to attempt this transformation using less inherently reactive compounds. We were pleasantly surprised to find that irradiation of 2 in cyclohexane solvent gave a single new hydride in high yield, and a similar result was obtained in neopentane solvent.

These products are the hydridoalkyl complexes 4 and 5 shown in Scheme 4.

Scheme 4



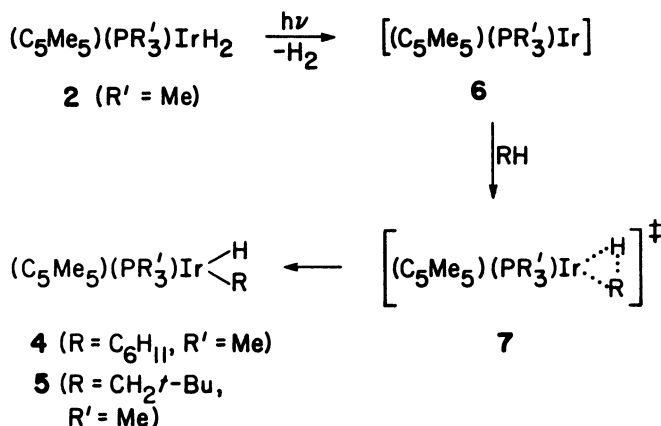
The new complexes are extremely hydrophobic, and are therefore very difficult to obtain pure. However, they can be isolated and purified with some loss of material, and characterized fully by ^1H NMR, ^{13}C NMR and infrared-alkyliridium derivatives (vide infra), which can be characterized using both spectroscopic and elemental analysis techniques (5). The hydrophobicity of these materials has so far prevented our obtaining X-ray quality crystals, but efforts in this direction are continuing.

MECHANISM OF THE C-H OXIDATIVE ADDITION REACTION

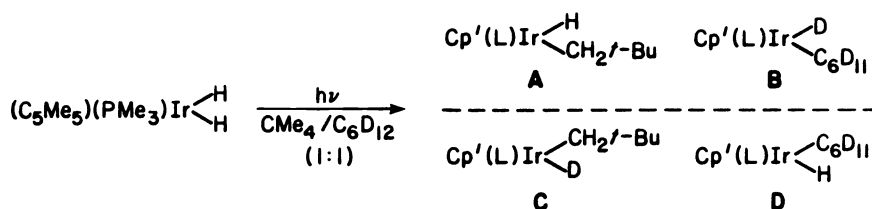
The conventional mechanism for the C-H insertion is shown in Scheme 5. It first assumes that upon irradiation, an excited state of dihydride 2 is formed. This rapidly extrudes H_2 , leaving behind the reactive, coordinatively unsaturated fragment 6. Complex 6 then inserts into a C-H bond via transition state 7, leading to the hydridoalkyliridium complexes 4 and 5.

Although this mechanism is reasonable, we felt the need to provide supporting evidence for it, especially in view of the fact that in certain other oxidative addition reactions more complicated mechanisms involving free radicals have been established (8). Many radical mechanisms proceed through a step in which the radical R^\cdot has independent existence. Thus the individual R and H groups located in each molecule of product 4 or 5 may not necessarily have been bound together in the starting hydrocarbon molecule. In order to obtain information about this, we carried out the crossover experiment summarized in Scheme 6. We first irradiated 2 in a 1:1 mixture of neopentane and cyclohexane. This established that the two hydrocarbons have similar reactivity toward 6, although the C-H bond in neopentane is slightly more reactive. Next, irradiation of 2 in a 1:1 mixture of

Scheme 5



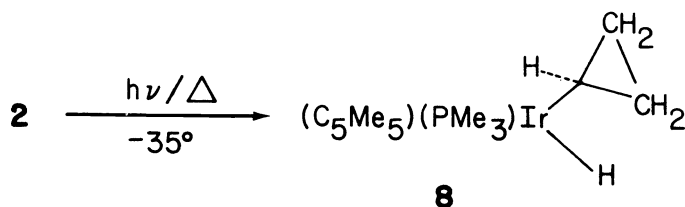
Scheme 6



neopentane and cyclohexane- d_{12} was carried out. As shown in Scheme 6, the products of this reaction were the hydridoneopentyl- and the deuterio-(perdeuterocyclohexyl)iridium complexes **A** and **B**, with very small amounts of contamination from the crossed products **C** and **D**. Therefore, the R and H groups remain associated with one another during the process which converts hydrocarbon to hydridoalkyliridium complex.

While this experiment rules out reactions involving radicals having a free existence and finite lifetime, it is more difficult to rule out processes proceeding predominantly through caged radical pairs. Our best evidence against such a postulate comes from relative reactivity studies. Hydrogen abstraction reactions of radicals favor C-H bonds with low bond energies; very strong bonds are nearly always inert. In view of this, cyclopropane may be used as a diagnostic substrate, since its C-H bond energy is 106 kcal/mole, even stronger than that of methane (9). Despite this, as shown in Scheme 7, irradiation of **2** in liquid cyclopropane at -35°C . leads only

Scheme 7

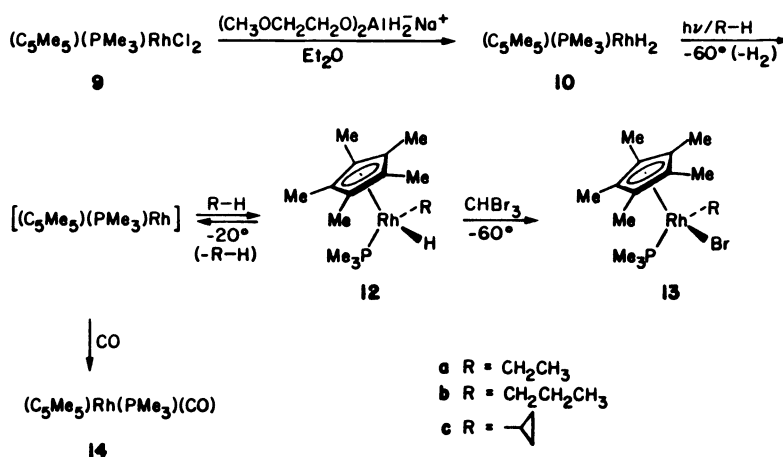


to the C-H insertion product **8**. Thus addition to the C-H bond is favored even over insertion into the relatively weak C-C bond, which would lead to an iridacyclobutane complex. In view of this result, even a radical-cage mechanism seems extremely unlikely for these reactions.

C-H OXIDATIVE ADDITION USING RHODIUM COMPLEXES

In light of the iridium chemistry summarized above, both Jones' group (10) and our own have been independently examining the related rhodium system ($\eta^5\text{-C}_5\text{Me}_5$)Rh(PMe₃)₂H₂ (complex 10 in Scheme 8) because of the possibility that selectivity and alkyl group functionalization will be enhanced with rhodium. Dihydride 10 was prepared (10,11) in 85% yield and analytical purity as shown in Scheme 8. Irradiation of 10 at room temperature resulted in loss of H₂ and formation of a dark, as yet unidentified product (presumably a cluster complex), but no new hydrides. However, when irradiation was carried out below -30°, the formation of new alkyl hydrides 12 (Scheme 8) was observed by ¹H NMR. As with iridium, this is a completely

Scheme 8



general reaction, occurring with all substrates we have tried which remain liquid at the temperatures required to maintain the stability of the hydridoalkyl complexes. Once again cyclopropane is an especially efficient substrate; the C-H insertion product is formed quantitatively on irradiation of 10 in this solvent, with no sign of any products formed by C-C insertion.

We have been able to characterize several of the hydridoalkyl complexes 12 by ¹H NMR, but all attempts at isolation have failed. However, treatment of the hydrides with a twofold excess of CHBr₃ at -60° converted them to the corresponding bromoalkylrhodium complexes 13. These, too, are sensitive materials, decomposing slowly in solution at room temperature or on attempted chromatography. However, in at least certain cases they can be isolated by rapid evaporation of solvent, extraction into n-hexane, and recrystallization from Et₂O/hexane. In this way pure samples of the bromoethyl (13a), -propyl (13b), and -cyclopropyl (13c) complexes have been obtained and characterized by elemental analysis and ¹H and ¹³C NMR spectroscopy.

The hydrido(aryl)rhodium complexes in this series are in general relatively stable. In contrast, the corresponding alkyl complexes are almost always less tractable, and before the work reported here was completed, none had been characterized by X-ray diffraction. For this reason, we made a particular effort to obtain X-ray quality crystals of one of the haloalkylrhodium complexes. After numerous attempts this was finally achieved in the case of the cyclopropyl complex 13c by slow recrystallization from a 25% mixture of THF in hexane. An ORTEP diagram is reproduced in Fig. 1; it shows clearly the intact cyclopropyl ring and its σ-bonding to the metal. Experimental support for a 3-center C-H oxidative addition mechanism analogous to that proposed for the iridium system (Scheme 5) is provided by the following experiments: (i) irradiation of 10 in a mixture of cyclopropane and perdeuterated methylcyclohexane resulted only in the formation of ($\eta^5\text{-C}_5\text{Me}_5$)-(PMe₃)Rh(C₃H₅)H and ($\eta^5\text{-C}_5\text{Me}_5$)(PMe₃)Rh(C₇D₁₃)D after 30% conversion of starting material; (ii) Low-temperature irradiation of 10 in solutions containing CO gave ($\eta^5\text{-C}_5\text{Me}_5$)Rh(CO)(PMe₃) (14); (iii) when a mixture of 10 and complex 12b was warmed to -20° in liquid cyclopropane, conversion of 12b to the corresponding hydridocyclopropyl complex 12c was observed.

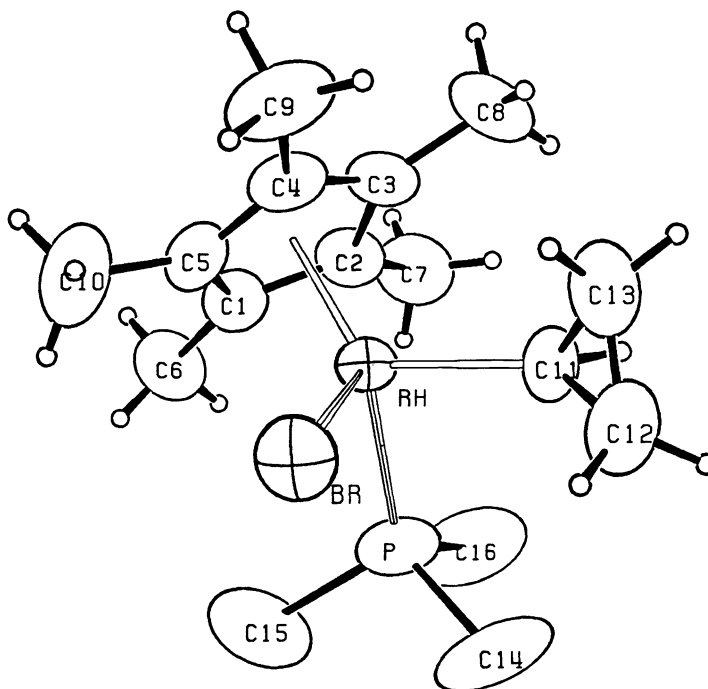
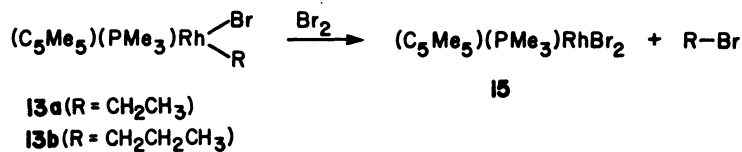


Fig. 1 ORTEP diagram of the molecular structure of $(C_5Me_5)Ir(C-C_3H_5)(Br)$ (13c).

FUNCTIONALIZATION REACTIONS

We have obtained some promising preliminary results on conversion of the alkyl groups in these rhodium complexes to organic molecules. In the iridium system we were not able to convert the haloalkylmetal complexes to organic bromides by direct treatment with Br_2 ; it was necessary to first effect alkyl transfer to mercury. In contrast, treatment of bromoalkyl-rhodium complexes 13a and 13b with Br_2 results in conversion to $(\eta^5-C_5Me_5)-(PMe_3)Br_2$ (15) and R-Br (Scheme 9) in high yield. We are continuing to

Scheme 9



search for other differences in functionalization behavior between rhodium and iridium, with a special eye toward finding reagents which will produce oxygenated derivatives.

OXIDATIVE ADDITION SELECTIVITY STUDIES

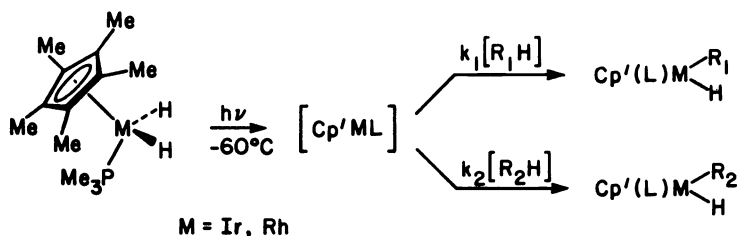
One of the most important questions we have attempted to address in our C-H activation work concerns the selectivity with which the iridium and rhodium reactive intermediates $(C_5Me_5)(PMe_3)M$ react with different types of C-H bonds. Irradiation of the corresponding dihydrides 2 and 10 in the presence of solvents having different types of C-H bonds allowed the reactive intermediate to compete for those bonds. Selectivities, or relative rates for insertion of the intermediate into the different types of C-H bonds present (k_1/k_2 ; cf. Scheme 10) can then be calculated from the yields of products formed, after statistical correction.

Two types of selectivity experiments were carried out: those involving competition of the intermediate for C-H bonds in different molecules

("intermolecular selectivity") and those involving competition for different types of C-H bonds located in the same molecule ("intramolecular selectivity"). Intermolecular selectivities can be established most readily, because each of the individual oxidative addition products can be independently generated. In addition, however, these experiments demonstrated that the hydridoalkyl products formed from similar types of C-H bonds exhibited ^1H NMR hydride resonances at chemical shifts that were very similar to one another, and quite well separated from those formed from different types of C-H bonds. For example, experiments with simple organic ring compounds established that insertion into secondary C-H bonds gave hydridoalkyliridium complexes with hydride chemical shifts between -18.16 to -18.67 ppm; in contrast, primary hydrides appear at substantially lower field, near -17.5 ppm. These shift dependences could be extended with significant self-consistency to substrates having more than one type of C-H bond. Thus both inter- and intramolecular selectivities could be established by simply integrating the hydride resonances in the NMR spectra of the C-H addition product mixture in each case, followed by statistical correction. Similar (although not quite so dramatic) trends were noted in the rhodium series, which was fortunate since the instability of the hydridoalkylrhodium complexes required that selectivity studies be carried out and analyzed at low temperature.

The selectivities for the rhodium and iridium intermediates, both measured at -60° in order to compare the two systems most carefully, are summarized in Scheme 10. The two reactive intermediates differ strikingly in their

Scheme 10



k_{rel} (Ir)	1.0	1.1	2.1	-	0.09	0.23	-	3.9
k_{rel} (Rh)	1.0	1.8	10.4	0.14	0.06	-	3.6	19.5
	Me_4C			$\text{CH}_2=\text{CH}_2$	CH_3-CH_3			
k_{rel} (Ir)	1.14	1.5	2.7*	-	-			
k_{rel} (Rh)	-	2.5(1.9)	5.9(2.4)	2.4	2.0			

*Primary C-H bond.

degree of selectivity. In all cases, the rhodium complex is significantly more discriminating, particularly between C-H bonds in the same molecule. Indeed, with acyclic alkanes the Rh complex apparently inserts only into primary C-H bonds, while the Ir complex favors primary insertion over secondary relatively weakly. In no instance has insertion into tertiary C-H bonds been observed for either system (12). The greater selectivity of the rhodium system (as well as the higher propensity of its hydridoalkyl complexes toward reductive elimination) correlates nicely with the presumably lower exothermicity of its C-H insertion reactions.

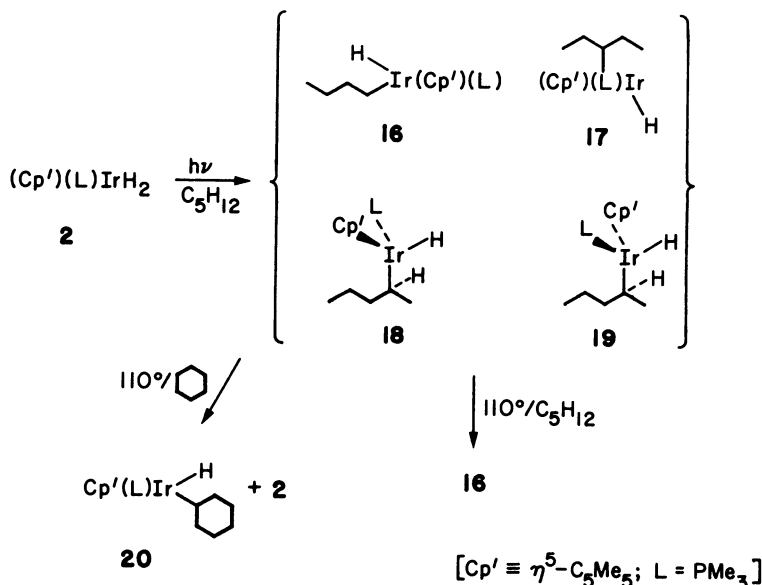
REVERSIBLE REDUCTIVE ELIMINATION/OXIDATIVE ADDITION STUDIES, AND THEIR USE IN THE ACTIVATION OF METHANE

Heating causes reductive elimination of alkane from $(\eta^5\text{-pentamethylcyclopentadienyl})(\text{trimethylphosphine})(\text{hydridoalkyl})\text{iridium}$ complexes, leading to an intermediate capable of undergoing oxidative addition to the C-H bonds in

other alkanes. We have used this property to establish reversible equilibrium between a pair of alkanes and hydridoalkyl complexes, allowing measurement of the equilibrium constant for this process and providing a method for determining relative metal-carbon bond energies. This chemistry has also allowed us to develop the first solution phase thermal oxidative addition of methane (13) leading directly to a stable hydridoalkylmetal complex.

The equilibration studies began with the mixture of dihydride **2** and alkyl hydrides (**16** - **19**) formed on irradiation of **2** in *n*-pentane. As illustrated in Scheme 11, heating this mixture to 110° in *n*-pentane caused disappearance

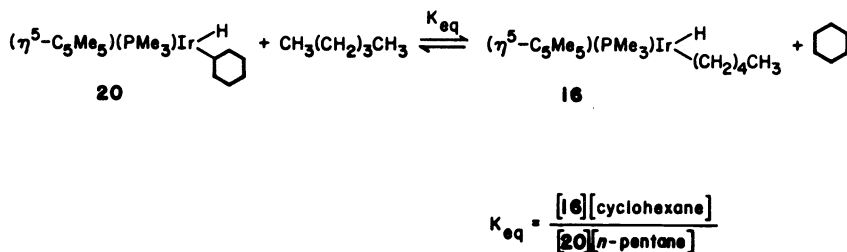
Scheme 11



of all the resonances in the ¹H NMR spectrum due to the secondary hydrides, and a corresponding increase in the signal due to the primary hydride. We judged from this observation that isomerization of secondary to primary hydridoalkyl complexes is possible by thermal activation at this temperature, and that (as expected (14)) the primary complex is thermodynamically more stable. Evidence that this isomerization occurs by intermolecular reductive elimination/oxidative addition was obtained by carrying out the reaction in cyclohexane, rather than pentane, solvent. In this case the amount of primary hydride remained constant, and the secondary hydrides were converted into hydridocyclohexyl complex **20** rather than primary hydrido-pentyl complex **16** (Scheme 11).

This experiment also suggests that the primary complex is stable to reductive elimination at 110°. In fact, higher temperatures are required to bring this material into the reductive elimination/oxidative addition equilibrium illustrated in Scheme 12. The equilibrium constant for this process

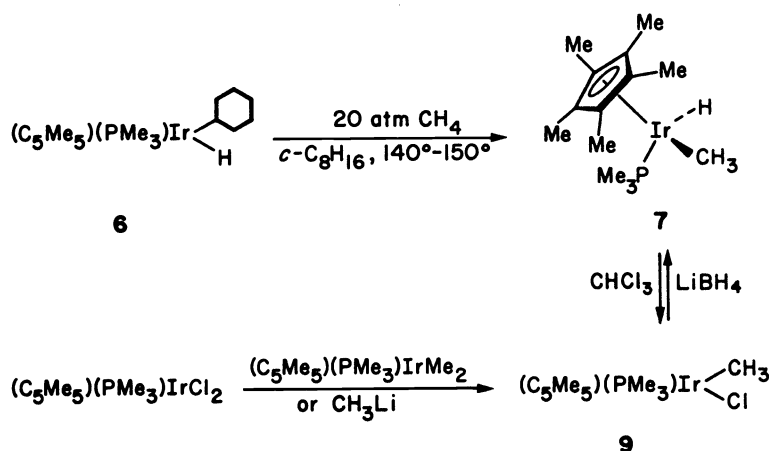
Scheme 12



can be conveniently measured by heating either the primary complex 16 or the hydridocyclohexyl complex 20 in a solvent mixture containing 91.5% cyclohexane and 8.5% n-pentane (15). With either starting material, equilibrium is reached after 50 h at 140°; the ratio of 16 to 20 under these conditions is 1.0 ± 0.1 . This allows calculation of an equilibrium constant of 10.6, which corresponds to $\Delta G^\circ_{\text{reaction}} = -2.0$ kcal/mole at 140°. Making the reasonable assumption that entropy changes for this reaction are small, and using 94.5 kcal/mole for the secondary C-H bond in cyclohexane and 98 kcal/mole for the primary C-H bond in n-pentane (16), we can calculate directly from this ΔG° that the metal-carbon bond energy in primary complex 16 is favored by 5.5 kcal/mole over the secondary metal-carbon bond in 20.

With the above results in hand, we have been able to achieve methane activation thermally and in high yield under reversible conditions by taking advantage of the presumption that the hydridomethyl complex 21 would also be thermodynamically very stable. Thus, as shown in Scheme 13 heating hydrido-

Scheme 13



cyclohexyl complex 20 in cyclooctane solvent in a sealed vessel under 20 atm of CH_4 at temperatures between 140° and 150° led to a 58% yield (^1H NMR) of hydridomethyl complex 21. Attempted isolation of the hydridomethyl complex by crystallization or chromatography proved difficult, as it has in the other cases discussed earlier, and so the material was treated with CHCl_3 , converting it to the corresponding chloromethyl complex 22, which could be purified and characterized by conventional means. The isolated yield of 9 from starting hydridocyclohexyl complex 2 was 50%. Confirmation of these structural assignments was obtained by independent synthesis: chloromethyl complex 22 was prepared by ligand interchange involving the corresponding dichloro and dimethyl complexes (Scheme 13); it was then converted to hydridomethyl complex 22 by treatment with LiBH_4 in diethyl ether. In the methane experiment, we assume that the hydridocyclohexyl complex 20 and the corresponding hydridocyclooctyl complex are formed reversibly, but do not build up due to their thermodynamic instability relative to the hydridomethyl complex 21; i.e., 21 is the "thermodynamic sink" for the system.

CONCLUSIONS

In summary, we have uncovered an example of the intermolecular reaction shown in Scheme 1, in which a soluble metal complex undergoes oxidative addition into the C-H bonds of completely saturated hydrocarbons, leading to hydridoalkylmetal complexes. Our most extensive work has been done with iridium, but the analogous rhodium complexes undergo similar C-H insertions, although the products are considerably less stable. We have found it possible to convert the insertion products into organic halides, indicating that overall conversion of alkanes into functionalized organic molecules is feasible. Selectivity studies have shown that insertion occurs most rapidly into aromatic, primary and small-ring C-H bonds, for both Rh and Ir, but the Rh system exhibits the higher degree of selectivity.

This work has raised many intriguing questions about the nature of C-H oxidative addition. First, we do not as yet understand why the systems discussed here seem to favor intermolecular addition, whereas other metal complexes either favor intramolecular cyclometallation, or do not react with unactivated C-H bonds at all. We also do not yet understand the physical basis for the selectivities we have observed. Finally, our results raise questions about the supposed requirement for a very electron-rich metal center in order to induce C-H activation. We have found that replacing PMe_3 with the more electron-withdrawing phosphine P(OMe)_3 gives a system which also effects oxidative addition. Independent work in Graham's laboratory demonstrates that even a CO ligand is not electron-withdrawing enough to prevent C-H insertion (17). We intend to seek answers to these questions in further research on this unique system.

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